

Chimia 46 (1992) 111–113
© Schweiz. Chemiker-Verband; ISSN 0009–4293

A Novel Cycloaddition Reaction of Thermally Generated Sulfenes

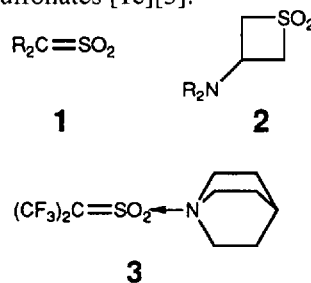
Ulrich Burger*, Serge P. Schmidlin, Jiri Mareda, and Gerald Bernardinelli

Abstract. The highly strained γ -sultine **4**, resulting from the addition of SO_2 to benzobenzvalene, is shown to undergo a thermal cycloreversion which gives 1*H*-indene-1-thiocarbonyl dioxides (**6**) as an intermediate and subsequently 1*H*-indene-1-carbaldehyde (**5**). The sulfene can be intercepted with electron poor C=C bonds in a cycloaddition process leading to a five-membered ring. The structure of the fused heterocyclic product **8b** resulting from addition of the sulfene **6** to *N*-phenylmaleimide was ascertained by X-ray analysis. Pent-4-enethial dioxides (**12**) produced by a sulfo-*Cope* rearrangement from allyl vinyl sulfone (**11**) is found to add to *N*-phenylmaleimide in the same 1,3-dipolar fashion as the sulfene **6**. The cycloadditions need not be *via* concerted pathways.

Introduction

Sulfenes **1** have been invoked, by analogy to ketenes, for many decades as reactive intermediates of the *tert*-amine-promoted HCl elimination of α *H*-alkylsulfonyl chlorides or of the complex reaction of SO_2 with diazoalkanes. Formal [2+2] cycloadditions with enamines giving amino-substituted thietane-*S,S*-dioxides **2**, or the addition of alcohols providing alkyl sulfonates, were purported to be characteristic sulfene reactions. The well-known formation of mesylates from mesyl chloride, the appropriate alcohol and a *tert*-amine normally follows this sulfene route rather than proceeding along an $\text{S}_{\text{N}}2$ pathway [1b]. The direct observation of a free sulfene remains elusive despite of the considerable efforts made so far [1]. Recent work suggests that the reactive species resulting from the *tert*-amine-promoted HCl elimination of α *H*-alkylsulfonyl chlorides is an amine-stabilized sulfene [2]. In corroboration, several quinuclidine bound sulfenes, e.g. **3** the adduct of bis(trifluoromethyl)sulfene [2c], have been isolated during the eighties with structural determination coming from X-ray crystallography. Some of these amine complexes react with enamines or with enol ethers in the afore-mentioned [2+2] fashion. With

alcohols the amine complexes react to give sulfonates [1c][3].



The introduction of a fluorodesilylation method by *Block et al.* [4] allowed the

in situ preparation of sulfenes in the absence of *tert*-amines. The reaction intermediate thus obtained unveiled, in addition to the reactions mentioned above, hitherto unknown dienophilic properties of the sulfenic C=S bond. For instance, it undergoes a clean *Diels-Alder* reaction with cyclopentadiene [4a].

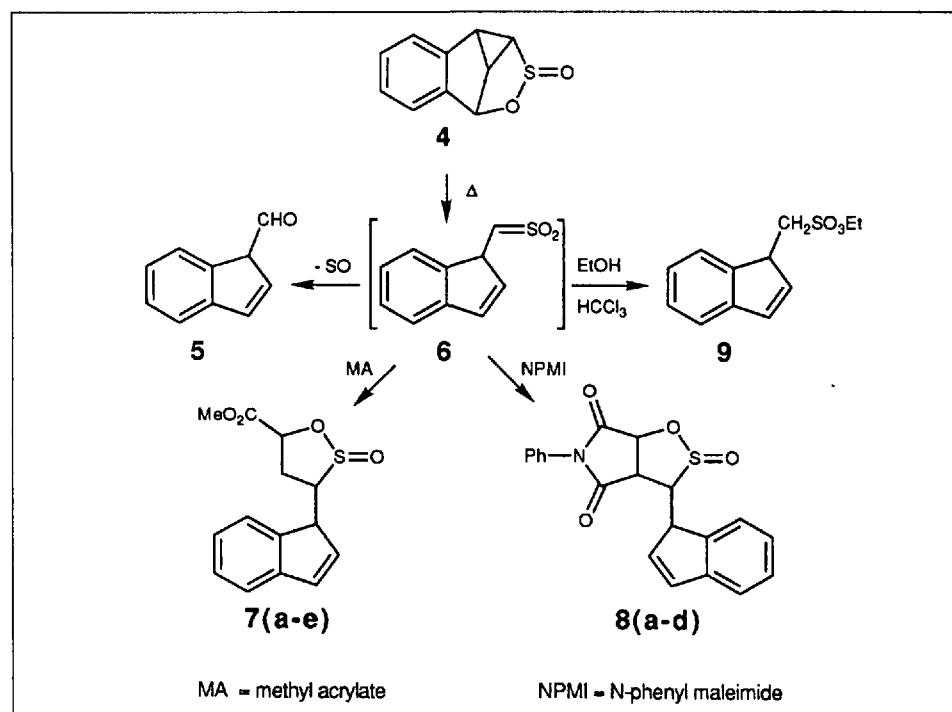
During our studies of thermal and photochemical transformations of strained cyclic sulfonates ('sultines') and of related compounds [5] we became aware of another, presumably genuine, sulfene reaction which to date has not been well studied. It consists of the addition of the reactive intermediate to electron deficient π -bonds, resulting in the formation of a five-membered ring. Overall, the reaction amounts to a cycloaddition with the sulfene being formally a 1,3-dipole.

Results

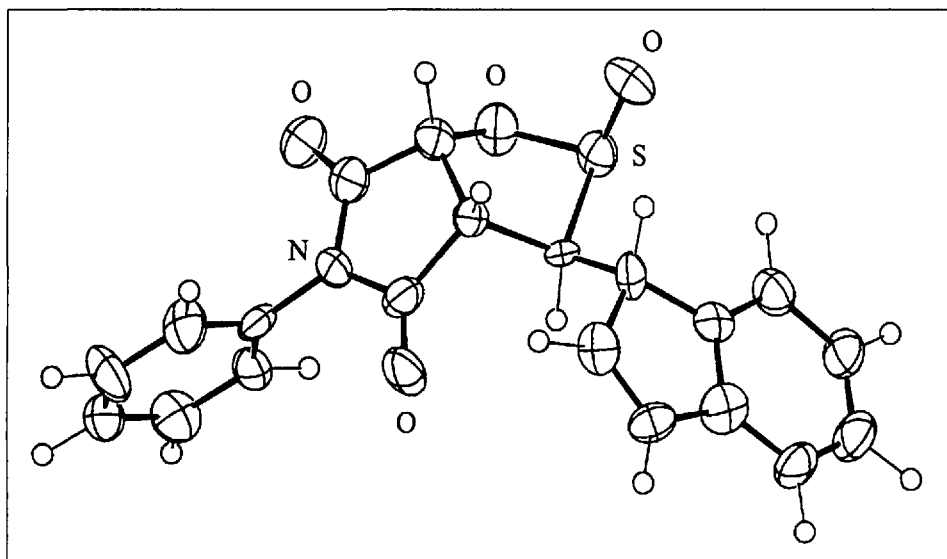
In a preliminary communication [5a], we have reported that the highly strained γ -sultine **4** resulting from the addition of sulfur dioxide to benzobenzvalene, gives 1*H*-indene-1-carbaldehyde (**5**) and naphthalene, both upon gas-phase pyrolysis (FVP at 380°) and upon heating in acid free CHCl_3 or CH_2Cl_2 (sealed tube, 120°) (Scheme 1). To account for this finding, ring opening of **4** was suggested to give the intermediate thiocarbonyl dioxides **6** which, upon loss of SO, could give **5**. Extrusion of SO with concomitant formation of a C=O function is a known thermal sulfene reaction [6].

The opening of **4** to give **6**, though not necessarily a concerted process, is remi-

Scheme 1



*Correspondence: Prof. U. Burger
Department of Organic Chemistry and
Laboratory of X-Ray Crystallography
University of Geneva
CH-1211 Geneva 4

Fig. 1. X-Ray crystal structure of the adduct **8b**

niscient of 1,3-dipolar cycloreversion reactions [7]. We attempted to intercept the intermediate **6** with dipolarophiles. Preference was given to π -electron deficient dipolarophiles due to the electronic nature of sulfenes (*vide infra*). When we heated the γ -sultine **4** in CH_2Cl_2 with excess methyl acrylate we obtained the stereoisomeric adducts **7(a-e)** in 58% total yield. However, none of them crystallized, and structural proof was limited to standard spectroscopic methods. We have been more successful with *N*-phenylmaleimide (NPMI) as the trapping agent. Four stereoisomeric adducts **8a-d** were obtained in 82% total yield (ratio **a/b/c/d** = 12:8:4:1). The second most abundant adduct **8b** was readily crystallized (m.p. 189–190°), and its structure was determined by X-ray diffraction [8] (Fig. 1). This now provides definitive proof for the formation of the ring system and, in addition, it reveals the relative configuration at the S-atom for this particular adduct.

It can clearly be seen in Fig. 1, that the sulfene moiety has added to *N*-phenylmaleimide with the formation of a five-membered ring. Both, the indenyl group and the exocyclic oxygen at the S-atom are oriented *trans* with respect to the N-containing ring.

According to IR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$ spectroscopy the isomeric adducts **8a**, **8c**, and **8d** contain the same fused ring system as **8b**, but their precise configuration is unknown at present.

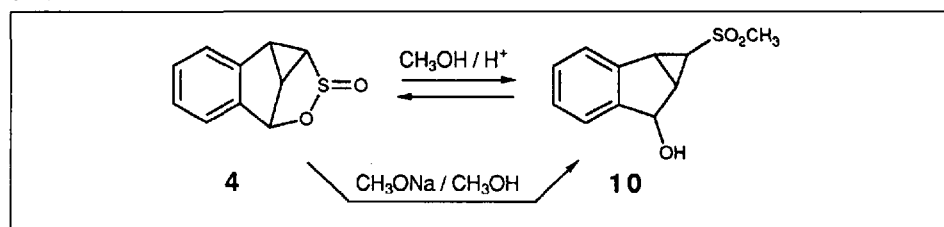
Our hypothesis that the γ -sultine **4** undergoes a thermal cycloreversion to give the sulfene **6** gains additional support from the trapping reaction with acid-free EtOH. Heating **4** in CHCl_3 with excess EtOH (sealed tube, 125°, 2 h) gives the sulfonate **9** in 87% isolated yield. It should be mentioned, however, that compound **4** reacts in a different manner with alcohols, if catalytic amounts of acid or base are

present. As shown in Scheme 2, ring opening occurs by direct attack at the S-atom of **4**. The reaction was found to be reversible when isolation of the ensuing sulfinate **10** by TLC on silica gel was attempted.

The thermal addition of a sulfene to an electron-deficient π -system in the previously discussed formal 1,3-dipolar fashion is to our knowledge without precedent, and so far it is an isolated case. The sulfene-type intermediates resulting from the HCl elimination of αH -alkylsulfonyl chlorides with *tert*-amines, which is normally performed at room temperature or

below, are reported not to react with acrolein or acrylates [1c]. Attempts in our laboratory to utilize *Blocks* fluorodesilylation method [4] to intercept the sulfene with acrylate have not met with success, as dimerization and oligomerization reactions prevail. We, therefore, looked for an alternative method to generate a *bona fide* free sulfene at high temperature. The [3,3]sigmatropic rearrangement of allyl vinyl sulfone **11** was chosen for that purpose. King *et al.* [1b][9] have demonstrated that **11** undergoes a sulfo-Cope rearrangement when heated with EtOH/pyridine (sealed tube, 175°) to give, *via* **12**, the pyridinium salt **13** (Scheme 3, path A). When we heated the compound **11** with a fivefold excess of *N*-phenylmaleimide (sealed tube, 175°, 6 h), we obtained the adduct **14** in 85% yield and virtually as a single stereoisomer (Scheme 3, path B). Compound **14** which is more sensitive to hydrolytic decomposition than the corresponding **8b** was isolated by medium-pressure chromatography on a short silica-gel column (AcOEt/hexane 1:1) and was fully characterized by standard spectroscopic means. We tentatively assign *trans*-orientation to the but-3-enyl side chain of **14** with respect to the N-containing ring. The configuration at the S-atom is unknown as yet. Anyway, **14** has the same fused heterocyclic skeleton as the compounds **8a-d** and certainly it has the same mechanistic provenance.

Scheme 2



Scheme 3

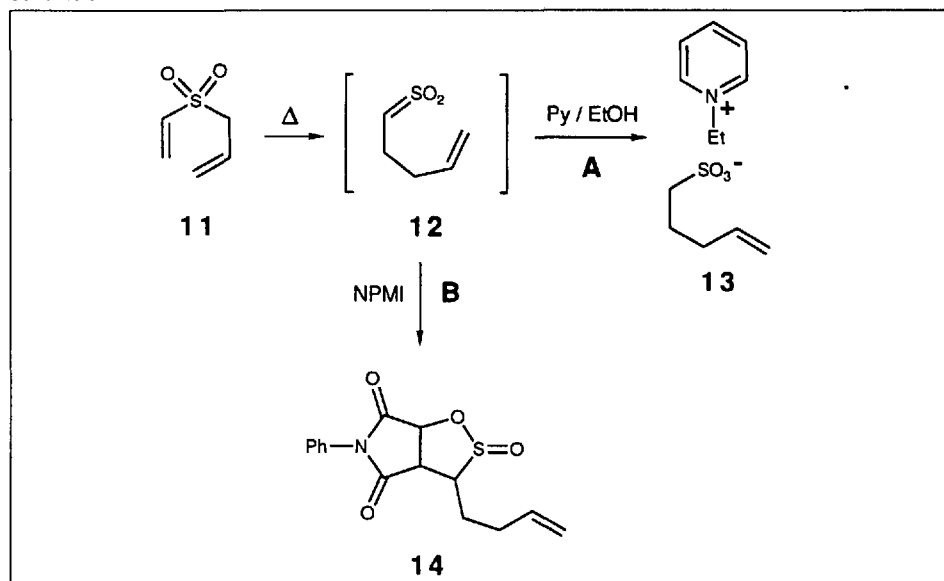


Table. Total Energies [au], Relative Energies^{a)} [kcal/mol]

| Molecule | Point group | STO-3G* Total energy | 3-21G* Total energy | Relative energy ^{a)} |
|---------------------------|-------------|-------------------------|------------------------|-------------------------------|
| Planar sulfene | C_{2v} | -579.394046 | -583.252583 | 0.0 |
| Twisted sulfene TS | C_{2v} | - | -583.177032 | 47.4 |
| Planar methyl sulfene | C_s | -617.979813 | -622.075470 | 0.0 |
| Twisted methyl sulfene TS | C_1 | - | -621.991090 | 53.0 |

^{a)} Relative energies are calculated separately for sulfene and methyl sulfene.

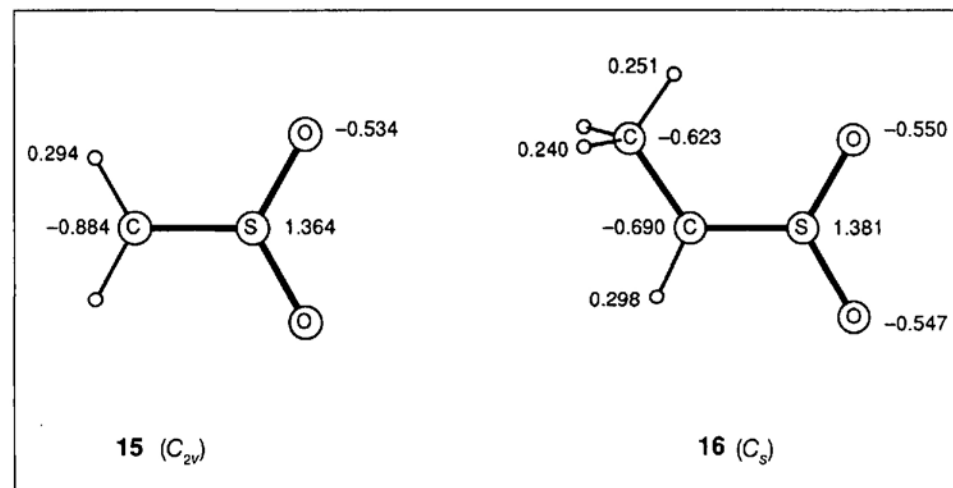


Fig. 2. Perspective drawings of the optimized structures for the planar sulfene **15** and methyl sulfene **16** together with their atomic charges (3-21G* basis set)

Discussion and MO Calculations

The electronic structure of the parent sulfene **15** (thioformaldehyde dioxide; $\text{CH}_2=\text{SO}_2$) has been the object of semiempirical MO calculations at varying degrees of sophistication (CNDO [10a], CNDO/2 [10b], and CNDO/B [10c]). However, nowadays it is well established that the participation of the d-symmetry functions in the bonding of second-row atoms should be included in the computations [11]. Such polarized functions are capable of reproducing more accurately not only the geometries but also the charge distribution. Therefore, we performed *ab initio* MO calculations using the GAUSSIAN-88 [12] system of programs. Geometries of all structures were optimized at the Hartree-Fock level with the STO-3G* [13] and 3-21G* [14] polarization basis sets. Two stationary points were located on the parent sulfenes potential energy surface, corresponding to the planar C_{2v} structure and the perpendicular C_{2v} rotamer. The vibrational frequencies analysis at the 3-21G* level permitted the characterization of the former as a global minimum, and the latter as a transition state for the rotation around the C-S bond (Table).

To assess the impact of alkyl substitution on the charge distribution in the sulfene, the *ab initio* computations have also been performed for the methyl sulfene

16 (thioacetaldehyde dioxide). The planar C_s structure has been found to be a minimum, whereas the twisted form is a transition state of C_1 symmetry with the rotational barrier of 53 kcal/mol (Table). Optimized planar structures of **15** and **16** together with the atomic charges are depicted in Fig. 2. For both compounds, it is worthwhile noting, that fairly large positive and negative charges are located on the S- and the C-atom, respectively.

The addition reactions of the thermally released sulfenes **6** and **12** to the electron poor double bonds of acrylate or maleimide with formation of five-membered rings need not be *via* concerted cycloadditions. We actually prefer interpretation in terms of a multistep process which starts by conjugate addition of the nucleophilic C-center of the sulfenes to the Michael acceptor.

The very large positive atomic charge on the S-atom accounts for the well-known electrophilic behaviour of sulfenes towards enamines and enol ethers, whereas the large negative charge on the C-atom and its concomitant nucleophilic features provide a good rationale for the cycloaddition described in the present work.

We thank the University of Geneva Computing Center for making available the computing resources of an IBM 3090-180 VF. Financial support was provided by the Swiss National Science Foundation (grant No. 20-27665.89).

Received: January 17, 1992

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